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THE POTASH CONTENT OF ILLINOIS SHALES

BY

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY MINER MANLY AUSTIN

ENTITLED The Potash Content of Illinois Shales

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
DEGREE OF Master of Arts

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*Required for doctor's degree but not for master's.

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I. GENERAL INTRODUCTION

The immediate purpose of this investigation has been to study the shales of Illinois with reference to their potash content and their adaptability to the manufacture of portland cement. However, as it has been our desire to add what we may to the tremendous amount of constructive effort now being expended by way of solving the present potash situation, it seems desirable to preface the discussion of our own work by a short summary of the results that have already been obtained along this line. Accordingly, the statistics relating to the production and consumption of potassium compounds will be given, and will be followed by a discussion of the most promising sources of potash that have been reported up to the present time.

II. IMPORTS AND PRODUCTION OF POTASH

In order to show the present trend of the potash situation in this country as well as to make more intelligible the data that will be presented further on in this paper, two tables have been prepared. Table I shows the importation of potassium salts during 1914, 1915, 1916 and 1917, while Table II gives some idea of the sources and of the amount produced in this country in 1917.

In connection with Table I attention is called to several points of interest. In the first place, during 1914 when conditions may be regarded as practically normal, the equivalent of 266,180 tons of K_2O was imported at an average price of \$46.5 per ton. The immediate effect of the war is clearly shown by the figures for 1915, while those for 1917 show that importations have practically ceased. It will also be noted that the price per ton during 1917 was about eight times normal. The data for production given in Table II is the latest obtainable. It was taken from the United States Geological Survey Press Bulletin for May 1918. This data shows that about two thirds of all potash produced came from natural brines. Kelp is the next highest contributor furnishing about one tenth, while distillery wastes, alunite, and cement dust follow in order. No other single source produced as much as one thousand tons. The total production was about one ninth of that imported in 1914. The average price per ton was a little less than ten times as great.

From the data just given it appears that to meet demands, especially that of the fertilizer trade, which will grow

steadily more urgent as time goes on, we must increase production at least ten fold. The means by which this may possibly be brought about will now be taken up.

TABLE I

IMPORTATIONS OF POTASSIUM COMPOUNDS SINCE 1913
(Tons of 2000 lbs.)

1914¹

	<u>Tons K₂O</u>	<u>Value</u>	<u>Price Per Ton K₂O</u>
Kainit	73,000	\$2,579,619	\$35.4
Potassium Chloride	166,000	7,925,781	47.8
Potassium Sulfate	27,150	1,887,491	69.5
Total	266,150	\$12,392,891	Av. \$46.6

1915¹

	<u>Tons K₂O</u>	<u>Value</u>	<u>Price Per Ton K₂O</u>
Kainit	9,780	\$444,996	\$45.6
Potassium Chloride	64,800	3,660,353	56.5
Potassium Sulfate	11,700	1,071,623	91.7
Total	86,280	\$5,176,972	Av. \$60.0

1916¹

	<u>Tons K₂O</u>	<u>Value</u>	<u>Price Per Ton K₂O</u>
Kainit	8	\$1,795	\$224.3
Potassium Chloride	1,340	466,888	348.0
Potassium Sulfate	1,310	197,808	151.0
Total	2,658	\$666,491	Av. \$251.0

1917²

	<u>Tons K₂O</u>	<u>Value</u>	<u>Price Per Ton K₂O</u>
Kainit	----	----	----
Potassium Chloride	490	\$209,300	\$427.5
Potassium Sulfate	95	22,950	241.5
Total	585	\$232,250	Av. \$397.0

TABLE II

POTASH PRODUCED IN THE UNITED STATES IN 1917³

Source	Tons K ₂ O	Value	Price Per Ton K ₂ O
Natural Brines	20,652	\$8,219,912	\$398
Alunite	2,402	892,763	371
Dust from Cement Mills	1,621	700,523	432
Dust from blast furnaces	185	68,841	372
Kelp	3,572	2,114,815	592
Molasses residue from distilleries	2,846	1,130,907	397
Wood ashes	424	406,856	960
Sugar house waste	359	143,430	400
Miscellaneous	<u>305</u>	<u>113,875</u>	<u>373</u>
Total	32,366	\$13,791,922	Av. \$426

III. SOURCES OF POTASH IN THE UNITED STATES

1. Saline Lakes⁴

Our interest in the Saline lakes of this country is due to the fact that they are producing potassium salts in commercial quantities at the present time. It will be seen from Table II that these lakes produced in 1917 much more potash than all other sources combined

There are two main localities where these deposits are being worked, the Great Basin and Northwestern Nebraska. The deposits in the Great Basin consist of mixtures of sodium and potassium carbonate, sulfate and chloride intermingled with more or less earthy material. For the most part they are deposits which have resulted from the complete drying up of land locked bodies of water, and they are characterized by the fact that they carry a preponderance of sodium carbonate and only a little, usually not more than five per cent of, potassium salts. The largest concern operating in this district at the present time is the American Trona Corporation, which receives its material from Searles Lake. According to their own advertising material they are the largest single producers in this country and are prepared to furnish potassium chloride of from sixty to ninety-nine per cent purity. They do not say how much they are producing, but if the above statement is true, the quantity must be in excess of 32,000 tons K_2O annually for that is the quantity now being produced by one of the large Kansas works. Just how they are recovering the potassium salts does not seem to have been brought out clearly in the literature, but it seems that they have simply added some re-

finements to the method of recrystallization that they have been using in refining the sodium carbonate that they have been producing for some time. Surveys have pronounced the source of supply of potash in this region as inexhaustable. It is to be remembered, however, that the potash content of the raw material is so low that it would be practically impossible to operate at a profit with such prices as prevailed before the war.

The Kansas deposits are scattered over an area of 8000 square miles of the western part of the state. The salts are carried by brine soaked sands that underlie the hard-pan which forms the bottom of shallow lakes. The process of recovery consists in sinking a large number of small wells into the sand beneath the hard-pan, connecting a group of these wells to a pump and then pumping the brine for distances of from three to ten miles to the railroad. The brines consist of from two to fourteen per cent of solids, and the solids contain from eight to thirty-six per cent of K_2O . They are conducted from the pipe line into concrete reservoirs and are then concentrated as far as possible in Swenson triple-effect evaporators. The strong brine is then still further concentrated in a "concentrator" or finishing pan and finally reduced to complete dryness in a rotary kiln. At present no separation of the salts is being attempted as the mixture, containing up to 29.8 per cent K_2O , is very acceptable to the fertilizer trade and is marketed without further treatment. Figures published in the latter part of 1917 place the rate of production of that region at 2,666 tons a month. This would amount to 32,000 tons a year or about twelve per cent of the quantity imported in 1914. How long these deposits will hold out is not

definitely known, but estimates as to the amount which Jesse Lakes, the richest of the group, will furnish, show that they may not last long. Estimates put the total amount lying beneath this lake at 250,000 tons of K_2O , a quantity just a little smaller than that imported during 1914.

2. Kelp⁵

The giant kelps that cover many hundreds of acres along the Pacific coast have been looked upon even before the war as a very promising source of potash. In fact, the Pacific Mulch Company was organized in 1911 to produce potassium fertilizer from this source. Since the war broke out at least three new companies have entered the field and are now producing.

In the recovery of potash from the kelp the first step consists, of course, in harvesting it and bringing it in from the sea. Because of the tremendous amount to be handled and its wet heavy condition, this operation has presented some difficulties. It is now being accomplished more or less successfully by the use of large mowing machines and mechanical devices which mow it off below the water and rake it up onto barges. Once cut, the wet material is not always handled in the same way. The simplest process consists in drying the material first in the sun and then in rotary dryers and marketing the dried product as fertilizer. When only potassium salts are to be recovered the kelp is quite completely ashed in rotary dryers and the ash then leached with water. The Hercules Powder Company operating a large plant on the Pacific Coast is recovering both potash and acetone, or rather, potash and acetic acid which they convert into acetone. Their method is to grind the wet material to a jelly like mass and ferment it.

Acetic acid is formed by the fermentation and at the same time it seems that the slimy material coagulates and settles so that the solution containing the acid and the potash may be drawn off. The acetic acid is neutrallized with calcium carbonate and converted into sodium acetate with sodium sulfate. The solution is then evaporated down and the potassium salts separated by crystallization. Potassium compounds of eighty per cent purity are said to be obtained.

Data already given in Table II shows that the equivalent of 3,572 tons of K_2O was produced from kelp in 1917. There seem to be three limiting factors, though, that prevent future development. In the first place the supply of raw material is not unlimited, for although large fields exist off the Pacific Coast many of them are in the shallow waters near rock bound coasts which make harvesting difficult and landing impossible. That this is a real limitation is indicated by the fact that laws have already been enacted which regulate methods and conditions by which harvesting may be carried on. In the second place the large amount of water in the kelp makes recovery of the solids inherently expensive. Finally the industry is limited to a small section along the Pacific Coast where the kelp grows and freight charges practically limit eastern shipment to refined salts. So far, attempts to cultivate growths of kelp on the Atlantic Coast have not met with success.

3. Wood Ashes

A number of factors prevent wood ashes from ever becoming a real source of potash. Hard wood waste, which yields a much larger percentage of potash than does soft wood is coming to

be almost a negligible quantity. Soft wood waste when incenerated in the ordinary way leaves very little ash and even that that does remain has lost much of its potash by volatilization. Modern methods of lumbering have reduced very materially the amount of wood wasted, while at the same time processes have been devised which permit the utilization of what waste does occur in ways much more profitable than the recovery of potassium compounds.

4. Chile Saltpeter⁷

Very recent statements by C. M. Barton, Vice-President of the Du Pont Nitrate Company indicate that it may be possible to recover large quantities of potassium nitrate from the Chile nitrate imported into this country. Mr. Barton says that the Du Pont Company is now recovering annually 1200 tons of K_2O as potassium nitrate. Though the figures that he gives conflict somewhat, his estimate is that 720,000 tons might be obtained each year if all the potash could be separated from all of the nitrate mined. At present the Du Pont Company is separating one third of the total potash contained in the ore and is using five tenths per cent of the output of the Chile fields.

5. Alunite⁸

Alunite is a hydrated potassium aluminum sulfate occurring in considerable quantities in Utah and Colorado. So far no deposits have been located elsewhere. The mineral contains about ten per cent of potash and when simply roasted becomes suitable as a fertilizer material. When the finely ground material is treated with hot slightly acidified water all of the potassium and aluminum goes into solution leaving the silica and other insoluble matter behind. To recover potassium carbonate from this

solution the aluminum is precipitated by an "alkali potassium" compound, the sulfate with barium carbonate, and the resulting solution evaporated. Another process mentioned in the literature is to roast the mineral and then dissolve the potassium sulfate from the roasted material.

Table II shows that 2,402 tons of K_2O were produced from this source in 1917.

6. Potash as a By-product from Pig Iron Production⁹

The possibility that potash may be obtained as a by-product in the production of pig iron is one that looks more encouraging than any heretofore discussed. The problem has been worked upon by R. J. Wysor of the Bethlehem Steel Company and has been very fully treated by him in an article published in the Bulletin of the American Institute of Mining Engineers for January 1917. The significant facts and figures brought out in this article will be summarized briefly.

The the Bethlehem Steel Company, where Mr. Wysor is superintendent of blast furnaces, twenty-two pounds of potash are charged into the furnaces for every ton of pig iron produced. Most of the potash charged is contributed by the ore, but the amount carried in by the fuel and flux is not negligible.

The potash finds exist from the furnace by a number of channels but seventy-five per cent of it goes out as fume through the gas mains while twenty per cent is carried down in the slag. That carried down in the slage is, of course, lost beyond recovery. That going off as fume ought to be recoverable. At present 55.9 per cent of the total amount of potash charged is being removed by the wet washers while 11.2 per cent is escaping from the

stacks. Four and nine-tenths per cent of the total charged settles out in the stoves and boiler passes and represents all that is being recovered at the present time. It amounts to only about a pound of potash per ton of pig iron produced.

The problem to be solved, obviously, is the complete precipitation of the suspended matter in the furnace gases by some dry method. The Bethlehem Steel Company has installed Cottrell electrical precipitators in one or two of its units but has not made public the results obtained. It should be noted that the electrical precipitator besides saving the potash in a recoverable form leaves the gas hot and dry instead of cold and wet. This ought to prove a decided advantage in the utilization of this gas as fuel.

In order to give some idea of the amount of potash that may possibly be recovered in the pig iron industry we have made some calculations based on what seem to be rather conservative assumptions. The production of pig iron in 1916 was about 39,500,000 tons. Assuming that the raw material from which this iron was produced carried 22.4 pounds of potash per ton of iron, and that, in addition to that now being recovered be added that lost in the wet washers, but not that escaping from the stacks, then it should be possible to produce 27,000 tons of K_2O annually from this source. Assuming 60.8 per cent recovery of the 22.4 pounds of potash charged with each of pig iron, then with pig iron at \$14.50 per ton and potash at \$46.60 as it was in 1914, the value of the potash saved would amount to 2.19 per cent of that of the iron produced. With iron at \$20.00 and potash at \$251 as they were in 1916 the potash would represent 8.5 per cent of the

value of the iron.

Taken all in all the field looks promising.

7. Potash from Cement¹⁰

That potash might become a by-product from portland cement manufacture seems first to have been suggested in 1912 by F. G. Cottrell. In an address before the New York meeting of the American Institute of Mining Engineers in February of that year he reported the results of his work on the abatement of the dust nuisance at the plant of the Riverside Portland Cement Company and mentioned, simply as a matter of interest, that the dust collected contained considerable amounts of water-soluble potash. Since that time the idea has been taken up by a number of cement companies and is now quite fully developed. The pioneers in the field were the Riverside and Security Cement Companies. They were the first to recover potash at their plants and have been among the most active in developing better methods. At the present time eight plants are said to be recovering potash.

The general theoretical considerations involved in the production of potash from cement are simple. At the temperatures reached in the kiln the potash which the raw material contains is volatilized and passes out as a fume with the burned gases. The dust and fume is precipitated from these gases by some appropriate means and the potash is leached from it. In practice, however, a number of difficulties have been encountered.

In the first place not all cement material now being used contains enough potash to make its recovery practical. This point will be developed more fully later.

Secondly, the per cent of the total potash volatilized

in the kilns of the different plants of this country shows considerable variation. The United States Department of Agriculture has done a large amount of work on this subject and has found extreme cases where as little as 25 per cent was volatilized while in other cases as much as 95.6 per cent was driven off. The average for 113 plants in this country was 47 per cent. No striking relations between the methods of handling the material and the amount of potash volatilized were found. The average for all plants using the wet process was 46 per cent, while that for those using the dry process was 47. Little or no difference was noted between coal and oil fired kilns. No locality was found where the plants showed any marked difference in the average per cent of potassium compounds given off unless it be that of Utah, Colorado and California where slightly higher percentages were found.

Two successful methods have been devised to increase the volatilization. The Security Portland Cement Company uses common salt. One per cent of the amount of the total is ground with the raw mix and also with the coal. By this means they have increased the per cent of the total volatilized from 38 to 65. Huber and Reath are the authors for a method which makes use of calcium fluoride. The calcium fluoride reacts with the potassium in the mix to form potassium fluoride. The reaction does not take place until the temperature is considerably above the boiling point of potassium fluoride so that when it does take place the volatilization is very rapid. When the dust laden gases get into the cooler part of the kiln the potassium fluoride again reacts with the lime associated with it in the dust to form insoluble calcium

fluoride which remains behind in the filter cake when the potash has been dissolved out and may be returned to the kiln. Calcium chloride, sulfur dioxide and steam have also been tried, but without any marked success.

The problem of precipitating the dust seems to have been quite successfully solved by the application of the Cottrell electrostatic precipitator.

Some difficulty has been encountered in dissolving out the potash from the dust. It was found at the Riverside plant that only 55 per cent of the potash in the dust was being extracted where analysis showed that 90 per cent should be water soluble. The trouble was found to be due to the fact that a double sulfate of potassium and calcium formed, which was only slightly soluble in cold water.

Hot water was found to dissolve it readily however, and now 90 per cent extraction is being effected by carrying out the leaching at about 85°.

This extraction just referred to is carried out in tanks having a capacity of seven tons of dust. The dust is added to water heated by injecting steam and the batch is mechanically stirred. After about fifteen minutes the solid is separated from the solution by means of a filter press. The solution is run into open evaporating pans and as the salt crystallizes out it is raked out and more solution added. The salt, which is almost wholly the sulfate of potassium and sodium, is allowed to drain and then dried in rotary dryers.

Table II shows that the production of potash from cement in 1917 was 1,621 tons. The United States Department of Ag-

riculture has found that on the average for 113 plants in this country, 1.93 pounds of potash is volatilized for each barrel of cement produced. They estimate that 87,000 tons of K_2O escape from the kilns of this country annually. They also estimate that the recoverable potash from all plants amounts to 75,000 tons, or if those losing less than one pound per barrel of cement be neglected, 71,000 tons. These estimates are based on the actual amount now being volatilized which as has been stated amounts on the average to only 47 per cent. If the per cent volatilized might be increased by some of the methods suggested, to 66 per cent, as the workers at Riverside say we may reasonably expect, then the potash from the cement mills of this country would mount up in the neighborhood of 100,000 tons.

IV. INTRODUCTION TO PRESENT WORK

During this fairly complete review of the literature on the production of potash from cement, one noticeable fact has been the lack of any reference to the efforts on the part of any company to increase its potash output by using raw material of higher potash content. Neither has it been found that a survey of the cement resources of this country has been conducted with any special reference to the potash in them. It has seemed desirable, therefore, to determine what results might be expected of such a survey. Local interest has caused us to confine our study to the shales of Illinois.

The literature, as far as we can find, contains record of only eight analysis of Illinois cement material for potash. These analyses are given in Table III. Although they have not proven to be of special interest from the standpoint of potash content, they have been of some assistance in determining the value as cement material of the new shales analyzed.

During the course of the investigation shale was found that ran so high in potash that it became of interest for its potash content alone. Some work was then done on this shale to determine whether this potash could be obtained in soluble form.

TABLE III¹¹

Analyses of Illinois Shales

Location	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Ferric Oxide (Fe ₂ O ₃)	Ferrous Oxide (FeO)	Lime (CaO)	Magnesia (MgO)	Potash (K ₂ O)	Soda (Na ₂ O)	Igni- tion loss
Alton	63.36	15.43	1.80	4.02	0.93	1.58	3.28	0.56	6.99
Albion	59.34	15.36	3.26	3.84	0.76	1.82	3.82	0.80	7.89
Springfield	60.31	17.74	5.04	1.96	0.41	1.96	2.88	1.07	6.71
Edwardsville	63.43	16.89	1.52	4.24	1.00	2.11	2.03	0.20	5.97
Galesburg	63.62	16.28	3.02	2.90	0.63	1.44	2.60	1.50	5.88
Streator	59.86	17.43	1.42	5.10	1.05	2.32	2.80	0.18	6.35
Danville	64.09	14.16	2.65	3.16	1.69	1.64	2.90	0.77	6.47
Danville	58.52	15.67	4.99	3.37	1.05	1.45	2.94	1.48	7.72
Average	61.56	16.12	2.96	3.57	.94	1.79	2.90	.82	6.74

PLATE I.



LEGEND

PORTLAND CEMENT COMPANIES.

- S= Sandusky at Dixon.
- C= Chicago at LaSalle.
- GA=German American at LaSalle.
- M=Marquette at LaSalle.
- L= Lehigh at Oglesby.
- U= Universal at S. Chicago.

Scale: 0 10 20 30 40 50 60 70 80 90 100 Miles

V. METHOD USED

The shales were first analyzed for their potash content. Where this was found to be high enough to make the shale interesting, a complete rock analysis was run to determine as far as possible by that means, the adaptability of the material to cement manufacture.

Attempts were made to render soluble the potash in the high potash shale by sintering with a number of reagents and also by the use of slacked lime under steam pressure. Some effort was also made to determine the state of combination of the potash in this state.

VI. EXPERIMENTAL

1. Samples

Samples of raw shale now being used by the Marquette and German-American Cement Companies at La Salle, Illinois, and also some of the flue dust taken from the same plants were kindly furnished by the companies. Sample No. 16 was furnished Mr. Westhafer by a student, Ralph Gale. All other samples worked upon were from those furnished Mr. T. O. Westhafer by the Illinois State Geological Survey. They are said to be representative of the deposits from which they were taken. They will be described in the same way and the same numbers will be assigned to them as were used by Mr. Westhafer in reporting the work that he has done on them. In addition to a written description, a map, plate I, is added on which the localities are marked. The locations of the cement plants of the state will also be added to this map.

2. Analytical Methods

The potash determinations were made by the J. Lawrence Smith method using chloroplatinic acid. The rock analyses were made according to the methods outlined by R. K. Mead in his book, "Portland Cement". Fusions, sinterings, etc., were done in platinum crucibles but Royal Berlin porcelain ware was used in all other cases where platinum was specified. The reagents and analytical methods for the potash determinations were checked by a satisfactory analysis of a standard sample of shale furnished by the Department of Analytical Chemistry. Duplicate determinations were made in all cases except in the latter part of the work on

the solubility of the potash where in most cases, but one determination was made.

The treatment of the shale with lime under pressure was conducted in an autoclave fitted with a pressure guage and a thermometer. The sample was contained in a covered porcelain dish supported above the water in the autoclave. The dish was found to be somewhat attacked.

3. Shales and Flue Dust from Marquette and German-American Companies

Shales used in the raw mix and dust taken from the settling chamber at the Marquette and German-American plants located at La Salle were obtained and analyzed. The following data were obtained.

Marquette

	Shale	Flue Dust
Total K_2O	2.6	0.8
Total Na_2O	0.8	0.4

German-American

	Shale	Flue Dust
Total K_2O	2.4	2.01
Total Na_2O	1.2	0.73
Water Soluble K_2O		0.5

It is not to be inferred from the low potash content of the flue dust that potash is not being volatilized at these plants. On the other hand it is known from analyses made by the United States Department of Agriculture that the Marquette plant is securing 44.4 per cent volatilization, while that obtained at Ger-

man-American is only 24.5. It is of interest to note that the latter is the lowest secured by any of the 113 plants studied by the Department of Agriculture. The low potash content of the dust may mean that it was taken from a part of the dust catcher where only the heavier material is depositing or it may be that the lighter potash carrying dust is not being collected at all.

The point of interest to us is the relatively low potash content of the shale, which is 0.3 per cent lower than the average of those given in Table III and 1.0 per cent lower than the average for those that we have analyzed.

4. Analyses of Shales

The shales that we have analyzed have all been of a more or less carbonaceous nature. In fact the first samples studied carried enough oil to be of value for that alone. However, since the ash amounted to about forty per cent it seemed desirable to examine it with a view to its possible utilization. Since our interest was primarily in the ash, the shales were first ashed down and then analyzed. In recording the analyses in Table IV the percentage of ash is given first and is followed by the other factors which are referred to the ash as one hundred per cent. The ash determinations for the first five samples were made by Mr. Westhafer.

Another table, Table V, has been prepared which gives some figures bearing on the use of the shales as cement material. The ratio of silica to alumina which should be between 2.5 and 3.5 is given. The per cent of potash in the raw mix has been calculated on the assumption that one hundred parts of shale would have

Table IV

ANALYSIS OF ILLINOIS SHALES

No.	Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
2	75.0						3.6	0.8
6	38.5	60.0	22.6	9.6	1.6	0.9	2.4	0.4
7	42.8	60.1	23.3	9.6	0.7	0.9	2.4	0.4
10	87.3	61.5	18.7	6.5	0.9	1.8	5.7	0.6
11	85.5	66.0	17.8	6.5	0.2	1.3	5.0	0.7
14	66.5	59.0	18.7	5.7	4.9	0.9	3.1	1.4
15	39.0	60.3	22.6	11.8	0.4	0.8	2.5	0.4
16	85.0	54.8	19.9	7.7	4.0	2.3	3.9	1.2

Table V

FACTORS OF INTEREST IN CONNECTION WITH THE UTILIZATION OF SHALES AS CEMENT MATERIALS

No.	SiO ₂ Al ₂ O ₃	Per Cent K ₂ O in Raw Mix	Pounds per barrel 66.6 per cent volatilization
6	2.65	0.56	2.15
7	2.58	0.55	2.15
10	3.29	1.40	5.28
11	3.70	1.20	4.50
14	3.15	0.78	2.93
15	2.67	0.57	2.20
16	2.75	0.99	3.72

to be mixed with that amount of limestone equal to twice the sum of the per cent of silica, iron, and alumina. Finally the recoverable potash per barrel of cement has been estimated on the assumption that the only loss in burning would be that due to CO_2 , and that 66.6 per cent of the total potash is recoverable. That 66.6 per cent recovery might be expected seems justifiable in view of the results secured at the Security and Riverside Companies.

Shale No. 2

Sample taken in Schuyler County in the S.W.1/4, Sec. 23, T 2 W, R 1 W. Two feet of carbonaceous shale above coal No. 5.

Though this shale contains 3.6 per cent of potash which is rather high, it was not completely analyzed, and nothing can be said as to whether it would make cement material or not.

Shale No. 6

Sample of cannel coal or oil shale taken in Johnson County, N.W.1/4, Sec. 35, T 11 S, R 4 E. 42-inch bed sampled at outcrop.

Shale No. 7

The same as No. 6 except that it was taken by sampling a twenty ton pile that had been mined and dumped beside the outcrop.

The ash from neither of these samples is of any special value for its potash content. As far as chemical composition is concerned, it would make cement material. The high percentage of carbon remaining after the oil is removed might be a fuel factor in burning.

Sample No. 14

Taken in Moultrie Country near Lovington. Black roof slate from top of coal No. 6.

The ash from this shale contains 3.1 per cent of potash and should make a cement material as far as can be told from chemical composition. The shale would give a raw mix a little higher potash content than the average of those studied by the Department of Agriculture.

Sample No. 15

Sample taken from new shaft in same locality as No. 6 and No. 7. In this case a 1500 pound sample was taken about 1/4 mile from the outcrop. The analytical sample was taken from this large sample. The oil factors on this shale as determined by Mr. Westhafer are good. The analysis is practically the same as for Nos. 6 and 7. Its potash content is 2.5 per cent as compared with 2.4 per cent for six and seven. This rather close agreement seems to indicate that the potash content of a given formation is quite uniform.

Sample No. 16

Shale from slag dump at mine at Lincoln, Illinois. A more exact description is not available.

This shale is very high in potash and low in carbonaceous matter. The potash content is 3.9 per cent and the shale would give a raw mix of almost one per cent potash. The analysis shows the shale to be otherwise adapted to use as cement material.

This shale is sufficiently near a cement manufacturing center to make it of interest as a possible component in the mixture for the potash output which might thus become available.

Sample No. 10

Sample taken on Caney Creek, south of railroad tracks and 3 miles N.W. of Jonesboro in S.W. 1/4, Sec. 11, T 12 S., R 2 W., third P.M. On creek going S.W. at least 35 feet of chocolate colored and black shale or slate. Sample 10 is a section of the lower 10 feet of this bed.

This shale contains 5.7 per cent potash and is the best in this respect of any analyzed. It contains but 12.7 per cent of carbonaceous matter and its composition is within the allowable limits of a shale that may be used as cement material. It would give a raw mix containing 1.4 per cent potash which is 0.2 per cent higher than the highest in use any where in this country as determined by the United States Department of Agriculture. Based on a recovery of 66.6 per cent it would yield 5.28 pounds of K_2O per barrel of cement. At 21.3 cents a pound which was the average for 1917 this would amount to about \$1.10 per barrel of cement produced. Attempts which were made to render soluble the potash in this shale will be taken up later.

Sample No. 11

Sample taken from the upper 25 feet of the deposit described in No. 10.

The composition of this shale differed from No. 10 in two factors. The potash content was only 5.0 per cent and the

silica was 63.0 as against 61.5 for No. 10. The analytical samples in both cases were taken from samples of only 50 pounds and it is possible that sample No. 11 runs abnormally high ^{in silica} due to the presence of sandy material in it. If the composition is representative of the deposit the silica alumina ratio is higher than it should be for a cement shale. The per cent of potash in the raw mix would be 1.2 and the recoverable potash per barrel of cement 4.5 pounds.

5. The State of Combination of the Potash in Sample 10

In an effort to determine the state of combination of the potash, a sample of the shale was sent to W. H. Tomlinson, Petrological Laboratory, Swarthmore, Pa., who prepared a thin section. This section was examined for us by L. E. Kennedy of the Department of Geology of the University of Illinois. The shale proved to be so fine grained that its make up could not be very definitely determined. Although it contains some feldspar, it does not appear that all of the potash is so combined. No other undecomposed potash bearing mineral could be detected.

It seemed possible that the potash might be held as the hydrous iron potassium silicate, glauconite¹². In that case both the iron and the potash ought to come out together when the shale was treated with acid. Accordingly two grams of shale were treated with 20 cc. of concentrated hydrochloric acid and warmed over the steam bath for one hour. The insoluble residue was filtered off, the iron was precipitated with ammonia, filtered, redissolved and titrated, and the potash was determined in the filtrate from the iron. 1.9 per cent of potash and 5.6 per cent of iron calculated

as Fe_2O_3 was dissolved. The composition of glauconite, according to Dana is not sufficiently constant to justify any calculations of the potassium iron ratio. These results indicate, however, that one third of the potash and 86 per cent of the iron is in some form that is rather readily attacked by acids. The fact that lime under pressure removed almost one third of the potash in one hour whereas only 44 per cent was removed by continuing the heating for four hours also indicates that part of it is more loosely held than the rest.

6. Efforts to Render Soluble the Potash In Sample 10

One gram of the shale was treated with 20 cc. of 10 per cent HCl and warmed over the steam bath for one hour. Heavy metals were precipitated from the solution with ammonium hydroxide and ammonium carbonate and the potash determined. The potash dissolved was 1.24 per cent or 21.8 per cent of the total.

Two grams of the shale was heated over the blast lamp in a platinum crucible for 15 minutes and then quenched with water. The sample fused a little on the bottom. When removed, ground and treated with HCl as above, no potash was dissolved.

One gram of shale was treated with 20 per cent of CaCO_3 over a good Bunsen burner. The sample did not fuse. Treatment with HCl as above dissolved 0.35 per cent of potash.

One gram of shale was heated with 0.25 gms. of CaSO_4 to just below fusion point for one hour. The sintered mass was ground fine and extracted with 200 cc. of hot water. Practically no potash was dissolved.

It is evident from the foregoing tests that heating

alone, or heating with calcium carbonate or sulphate does not change the shale in such a way as to make the potash more easily soluble.

Several tests were made to determine what effect lime under steam pressure would have on the shale. Three determinations were made using lime and shale in the proportion to form cement mix, that is one gram of shale and 1.85 grams of lime. A fourth determination was made using twice the proportion of lime and carrying out the test on ten grams of shale instead of one gram as was done in the first three cases. All of the tests were carried out by heating in an autoclave at about 150 pounds pressure.

In the first three cases one determination of the potash was made on the washings from the whole sample. In the fourth case the mixture was washed with 800 cc. of hot water and after diluting to one liter, two 100 cc. aliquot were analyzed. The following data were obtained:

Shale	Lime	Time	Potash dissolved	Per cent of total potash
1 gr.	1.85 gr.	1 hr.	1.78 per cent	31.3
1 gr.	1.85 gr.	3 hr.	2.15 per cent	37.8
1 gr.	1.85 gr.	4 hr.	2.54 per cent	44.6
10.0 gr.	37.0 gr.	5 hr.	2.58 per cent	45.2

These results show that most of the potash that can be dissolved by lime under these conditions comes out in the first hour. Solution seems to have taken place more slowly after that length of time and becomes very slow after four hours. The increased concentration used in the fourth test did not increase the amount dissolved to any extent, and it seems that for the pressure used we have reached a limit at 45 per cent of the total. Theoretically an increase in the pressure, or rather an increase in

the temperature which is the influential factor, ought to increase the rate of solution. Whether it would increase the amount that could be dissolved is somewhat doubtful as the rate of solution at 150 pounds pressure, after 44 per cent has been dissolved, seems to be very slow.

VII. SUMMARY AND CONCLUSIONS

1. Shale used by the Marquette, and German-American Cement Companies at La Salle, Illinois have been analyzed for potash.

2. Eight other shales have been studied. Complete rock analyses have been made on seven of these.

3. Attempts have been made to determine the state of combination of the potash in high potash shales, and to obtain the extraction of this potash in soluble form.

4. Shales occur in one locality in Illinois in deposits approximately 35 feet thick which contain 5.0 - 5.7 per cent potash. These shales are suitable as far as chemical composition is concerned to use in the manufacture of portland cement.

5. About one third of the potash in the high potash shale is rather loosely held. Thirty-three and 3 tenths per cent of the total may be brought into solution with concentrated hydrochloric acid. Forty-five per cent may be dissolved out by means of lime under steam pressure.

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